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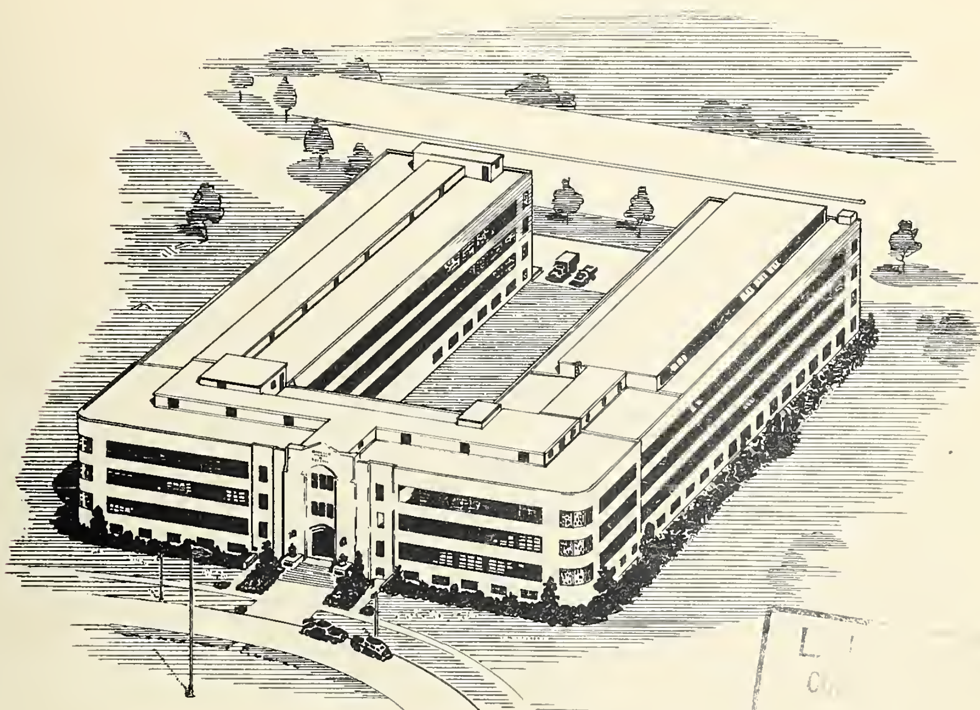
SCRUBBING NICOTINE FROM STEAM



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SCRUBBING NICOTINE FROM STEAM*

J. B. Claffey[1], E. O. Strolle[1], G. W. Macpherson Phillips[2] and Roderick K. Eskew[3]

INTRODUCTION

Nicotine has been used as an insecticide for many years. Despite the introduction of many new competitive insecticides during the past several years, there is still a definite place for nicotine. During the war years (1941-1945), the supply of nicotine was considerably below the demand. The U. S. Department of Agriculture is studying *Nicotiana rustica* to determine whether it could augment the supply of nicotine in our country. *N. rustica* usually has a higher nicotine content than most American tobaccos. It contains 6 to 8 percent nicotine (moisture-free basis), which under favorable conditions might warrant growing the crop as a source of nicotine. As part of the over-all program, experiments have been made at this Laboratory to develop processes for recovering nicotine from *N. rustica*. The information obtained in this work is also applicable to the recovery of nicotine from tobacco.

Published information on nicotine processing is scarce. Kingsbury et al.[4] have developed a process for recovery of nicotine from the exhaust gas of a tobacco re-drier in which the gas is scrubbed with water and nicotine is extracted from the dilute aqueous solution by ion exchange. Nicotine can also be recovered from dilute aqueous solutions by a two-step liquid-liquid extraction process. In the first step, nicotine is extracted from water by kerosene, as shown by Claffey et al.[5] or by other solvents, as shown by Badgett[6]. In the second step, nicotine is extracted from the kerosene by sulfuric acid[7].

The present paper describes some preliminary experiments on recovery of nicotine by scrubbing it from steam with sulfuric acid. In such a process, the vapor entering the scrubber would be obtained by steam distillation of tobacco waste or *N. rustica*. In either case, the vapor would contain about 0.6 percent nicotine; the remaining 99.4 percent would be steam with a trace of ammonia and some dust. This vapor would be treated with sulfuric acid to form the nicotine sulfate of commerce, which usually contains 40 percent of the alkaloid.

* Report of a study made under the Research and Marketing Act of 1946.

1 Chemical Engineer, Chemical Engineering and Development Division.

2 In Charge, Process Development Section, Chemical Engineering and Development Division.

3 Head, Chemical Engineering and Development Division.

4 Kingsbury, A. W., Mindler, A. B., and Gilwood, M. E., Chem. Eng. Prog. *44*, 497-500 (1948).

5 Claffey, J. B., Badgett, C. O., Skalamera, J. J., and Phillips, G. W. Macpherson, Ind. and Eng. Chem. *42*, 166-71 (1950).

6 Badgett, C. O. (In Press).

7 Unpublished results of work at this Laboratory.

The term "40 percent nicotine sulfate," as used [illegible] trade, might be more properly termed "52 percent nicotine sulfate." [illegible] actually a mixture containing 40 parts of nicotine combined with approximately 12 parts by weight of sulfuric acid in sufficient water to make 100 parts. In this paper, however, nicotine sulfate concentrations are expressed according to terminology common to the trade.

EQUIPMENT AND PROCEDURE

Packed Tower

Figure 1 shows a flow sheet of the scrubbing process. Synthetic mixtures of water and nicotine, or water, nicotine, and ammonia, were used as the starting material. This mixture provided a convenient source of vapor having the same composition as that evolved from steam distillation of tobacco waste or *N. rustica*, except for any entrained dust and tars. The container for the liquid was mounted on a platform scale, and the liquid was supplied by a metering pump of the diaphragm type. This type of pump had the minor defect of delivering a pulsating flow, but this was practically eliminated by a small surge chamber and a needle valve. The liquid then passed through a rotameter to a 5-square foot, multiple-tube vaporizer with liquid flow through the tube and steam on the shell side, which eliminated surging. About 96 percent of the liquid was vaporized; the remaining 4 percent dropped out in the separator. The vapor passed up through the scrubber and then to the condenser.

The scrubber was made from two pieces of glass pipe mounted concentrically; glass equipment was used so that the scrubbing operation could be observed. The inner pipe was 2-3/4 inches I.D. by 37 inches long and was packed with 3/8-inch ceramic Raschig rings. Three packing heights were used -- 11, 22, and 30 inches. The outer pipe was 4 inches I.D. Steam at 1.5 gage was admitted to the area between the two pipes to maintain a scrubbing temperature of 215° F. The temperature of both the entering vapor and the scrubbing liquid must be such that neither vaporization of the scrubbing liquid nor condensation of the vapor occurs. Vaporization of the liquid would undesirably concentrate the acid and condensation of the steam would dilute the acid. The boiling point of 20 percent sulfuric acid is 218° F. Consequently, in practical operation the average temperature in the tower must be maintained between 213 and 218° F. The outer pipe was insulated with a removable blanket. All acid lines were high nickel-copper alloy and were heavily insulated; a reheater should have been used, however, as later experiments showed that insulation was not sufficient to prevent some loss of heat from the system. The scrubbing liquid was 20.2 percent sulfuric acid solution. If a flow rate corresponding to the stoichiometric quantity were used, the rate would be only 1 pound per hour per square foot of tower for the vapor velocities used in these experiments, or so low that it would not wet the packing. Excess acid was therefore recirculated to the tower through an orifice meter. The stoichiometric concentration of sulfuric acid to produce 40 percent nicotine sulfate is 20.2 percent, but it would require 8 to 10 hours' continuous operation to completely convert the acid to nicotine sulfate. Experiments were therefore made with scrubbing liquid

containing various ratios of sulfuric acid and nicotine sulfate, corresponding to progressive stages in the complete cycle from 0 percent sulfate -- 20.2 percent sulfuric acid to 0 percent sulfuric acid -- 40 percent nicotine sulfate.

Each experiment was started with distilled water to bring the equipment to operating temperature, then was shifted to the synthetic mixture. Liquid that dropped out in the separator had the same nicotine content as the feed; hence the vapor entering the scrubber contained 0.58 percent nicotine. Fifteen-minute experiments were then made.

Samples of condensate from the condenser were collected at the start, middle, and end of the experiment, and the average nicotine analysis was used in calculating scrubbing efficiency. Analyses for nicotine were made by titration with 0.01 normal hydrochloric acid; methyl red was used as an indicator. Frequent checks were also made by the official method of the Association of Official Agricultural Chemists, in which nicotine is precipitated with silicotungstic acid. During the latter part of the program, a rapid and accurate method of nicotine analysis based on the ultraviolet spectrophotometer[8] was developed by C. O. Willits and his associates of this Laboratory.

Unpacked Tower

N. rustica and tobacco contain ammonium salts, and the ammonia evolved during steam distillation reacts with the sulfuric acid. Sometimes the amount of ammonium sulfate formed is in excess of its solubility. It is reported that in the commercial processing of nicotine from tobacco waste, the maximum concentration of nicotine sulfate that can be produced in the scrubber is about 10 percent. Attempts to exceed this concentration result in fouling the packing with ammonium sulfate, rendering the towers inoperative. Obviously, the amount of precipitated salt varies with many factors, including the temperature in the tower, ratio of ammonia to nicotine in the entering steam, concentration of sulfuric acid, nicotine sulfate in the tower, and the amount of entrained dust and tars. To eliminate the problem of fouling, experiments were made in unpacked towers.

Since in commercial practice, the vapor obtained from the steam distillation of dry plant materials would contain entrained dust, which is difficult to remove, in these experiments, we did not follow the customary practice of dispersing the vapor through a porous medium. Instead, the vapor was introduced through a pipe at high velocity directly into the bottom of the tower containing the scrubbing liquid. Experiments were made with scrubbing liquid containing 20.2 percent sulfuric acid, different percentages of which had been previously converted to nicotine sulfate.

8 Willits, C. O., Swain, M. L., Connelly, J. A., and Brice, B. A., Anal. Chem. *22*, 430 (1950).

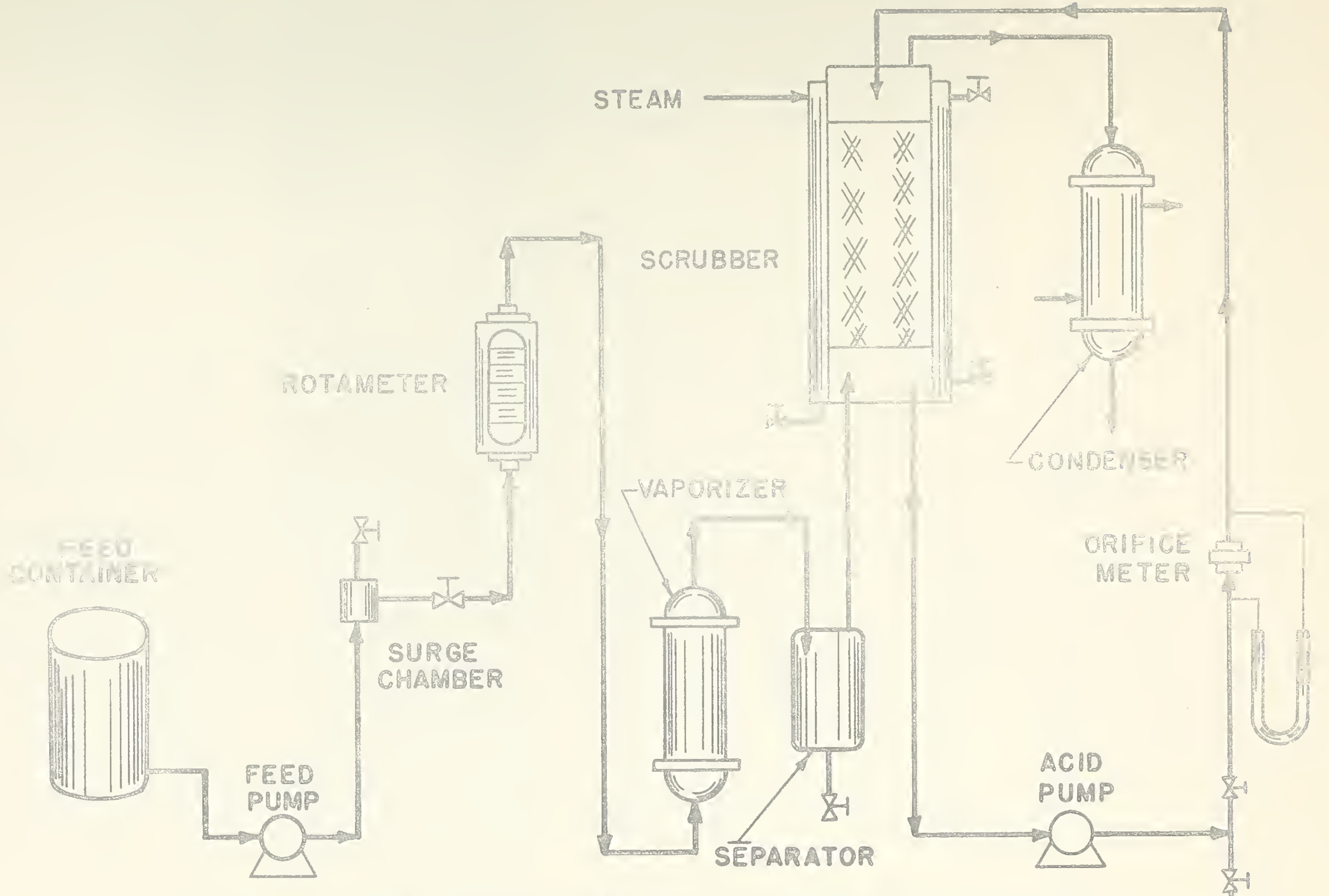

FIG.1– FLOW DIAGRAM OF SCRUBBING PROCESS FOR REMOVAL OF NICOTINE

RESULTS

Packed Tower

Table I shows the percentage of nicotine removed with different concentrations of acid. A vapor velocity of 1.2 feet per second (based on the total cross section of the tower) and 30 inches of packing were used in these experiments.

TABLE I

EFFECT OF CONCENTRATION OF SCRUBBING ACID ON REMOVAL OF NICOTINE

Scrubbing acid			Nicotine[1] in condensate		Nicotine[1] removed in scrubber	
Free H_2SO_4	Nicotine sulfate	Flow rate	(1)	(2)	(1)	(2)
%	%	lbs./hr./sq.ft.	%	%	%	%
20.6	0.0	322	0.00	0.0005	100	99.91
13.0	15.0	438	.00	.0002	100	99.97
5.3	30.0	460	.00	.0002	100	99.97
3.3	34.0	460	.008	.005	98.7	99.14

[1] (1) DETERMINED BY TITRATION; (2) BY ULTRAVIOLET SPECTROPHOTOMETER.

Figure 2 shows that the scrubbing efficiency was essentially 100 percent until the concentration of nicotine sulfate in the scrubbing acid increased to about 34 percent (3.3 percent free sulfuric acid) and that efficiency decreased sharply beyond this point. The process thus calls for two scrubbing towers in series; the second tower would merely act as a "catch-all" during 90 percent of the cycle, but during the last 10 percent of the cycle, it would do most of the scrubbing. Nicotine sulfate would be withdrawn as product from the first tower at the end of a cycle; acid from the second tower would then be transferred to the first one, and fresh acid would be pumped into the second tower.

To determine the packed tower requirements for effective scrubbing in the more difficult range beyond 30 percent nicotine sulfate in the scrubbing liquor, some experiments were made with different lengths of packing and different vapor and liquid flow rates. The scrubbing liquors contained 35 percent nicotine sulfate (2.8 percent sulfuric acid). Figure 3 shows the results. Nicotine removed at a vapor velocity of 1.1 feet per second was 99 percent with 30 inches of packing, 98 percent with 22 inches, and 96 percent with 11 inches. Thus scrubbing efficiency decreased only slightly with decreased height of the tower. The height of 11 inches is only 4 times the diameter; this is a shorter tower than is normally used in scrubbing.

With vapor velocity of 2.2 feet per second and 11 inches of packing, nicotine removal was only 75 percent with a flow rate of 460 lbs./hr./sq. ft. of scrubbing liquor, but removal was increased to 85 percent with 1200 and to 92 percent with 2740 lbs./hr./sq.ft. Removal of 92 percent would be adequate, since removal would be essentially 100 percent in the fore part of the cycle and the second tower would remove the remaining 8 percent. There was no sign of flooding, indicating that velocities in excess of 2.2 feet per second could have been used; however, the capacity of the vaporizer had been exceeded. Thus to obtain all the nicotine removal required in the first stage, for example, 92 percent, a tower only 4 times longer than its diameter would be adequate at a vapor velocity of 2.2 feet per second and a liquid flow rate of 2740 lbs./hr./sq. ft.

Unpacked Tower

Figure 4 shows the results of the experiments in the unpacked tower. By comparing this with Figure 2, it is apparent that at vapor velocities between 1.2 and 2.7 feet per second in the unpacked tower, nicotine removal never exceeded 97 percent even in a favorable range of sulfuric acid concentration, whereas in a packed tower essentially 100 percent was obtained until the sulfuric acid in the scrubbing liquor was reduced to about 4 5 percent. This slight difference in efficiency in the early stages of the cycle, however, became unimportant when two-stage scrubbing was used.

The pH of the scrubbing liquid containing 40 percent nicotine sulfate was 5.1. The pH of the finished product should be about 6, since it is corrosive to the shipping containers at a lower pH. It would thus be necessary to adjust the pH from 5.1 to 6 by the addition of a suitable alkali.

The effect of ammonium sulfate on efficiency of scrubbing was shown by two pairs of experiments. In the first pair, the scrubbing liquid contained 5.0 percent sulfuric acid and 30 percent nicotine sulfate. In one case, 15 grams of ammonium sulfate was added per 100 grams of liquid, and in the other case no ammonium sulfate was added. The presence of the salt reduced nicotine recovery from 96 percent to 94 percent.

In the second pair, the scrubbing liquid contained 1.0 percent sulfuric acid and 38 percent nicotine sulfate. When no ammonium sulfate was added, the nicotine removal was 85 percent, but it was 78 percent when 15 grams of ammonium sulfatewas added per 100 grams of scrubbing liquor.

The ratio of ammonia to nicotine in the vapor from the still can be expected to vary according to the raw material. The ratio is about 1 to 10 in *N. rustica*. A final pair of experiments was made in which vapors containing 0.054 percent ammonia and 0.54 percent nicotine were passed through a scrubbing liquid containing in one case 5.0 percent sulfuric acid and 30 percent nicotine sulfate. In the companion experiment 15 grams of ammonium sulfate was added per 100 grams of the scrubbing liquid. Addition of the ammonium sulfate reduced the nicotine removed from 97 to 94 percent. In all the foregoing experiments, the ammonium sulfate remained in solution.

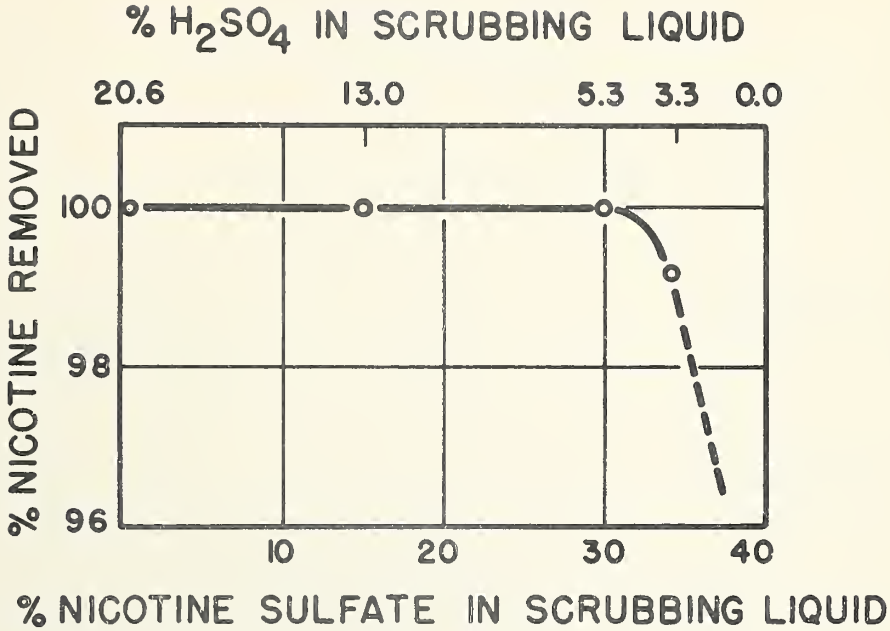

FIG.2—EFFECT OF CONCENTRATION OF SCRUBBING ACID ON REMOVAL OF NICOTINE (PACKED SCRUBBER OF $2\frac{3}{4}$" I.D.)

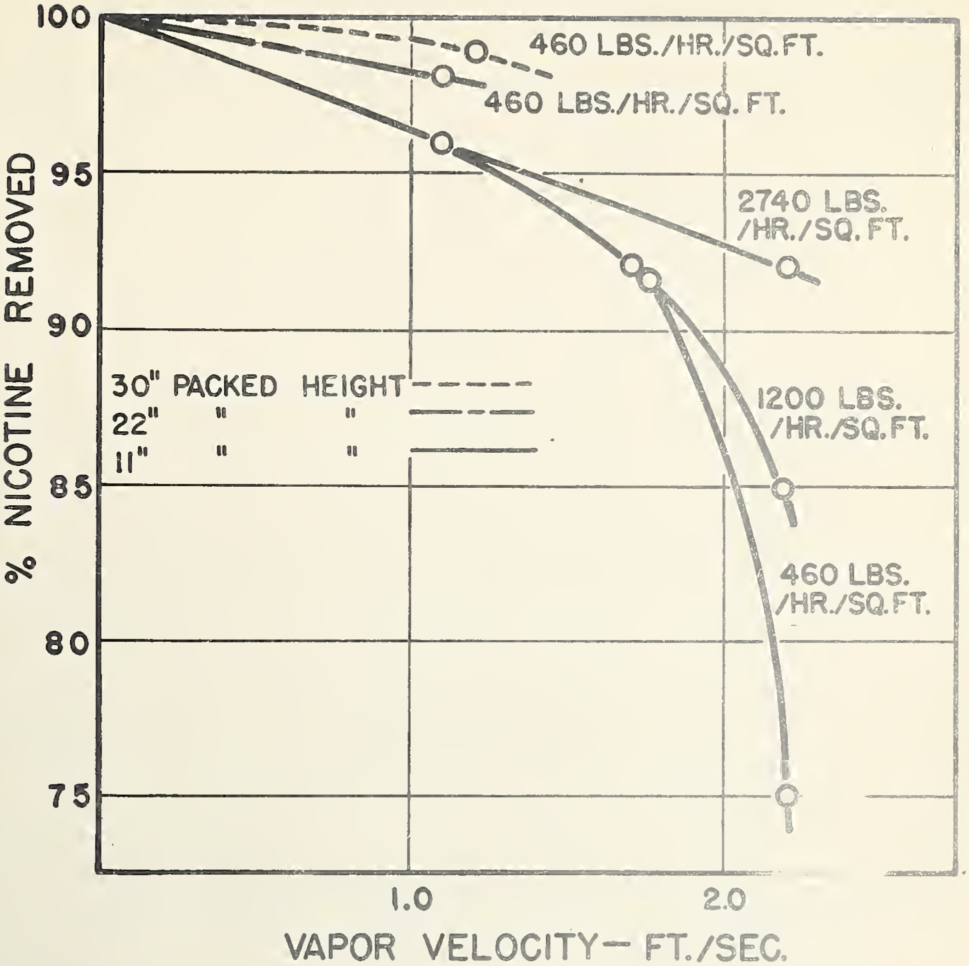

FIG. 3-EFFECT OF VAPOR VELOCITY ON REMOVAL OF NICOTINE (PACKED SCRUBBER OF $2\frac{3}{4}$" I.D.)

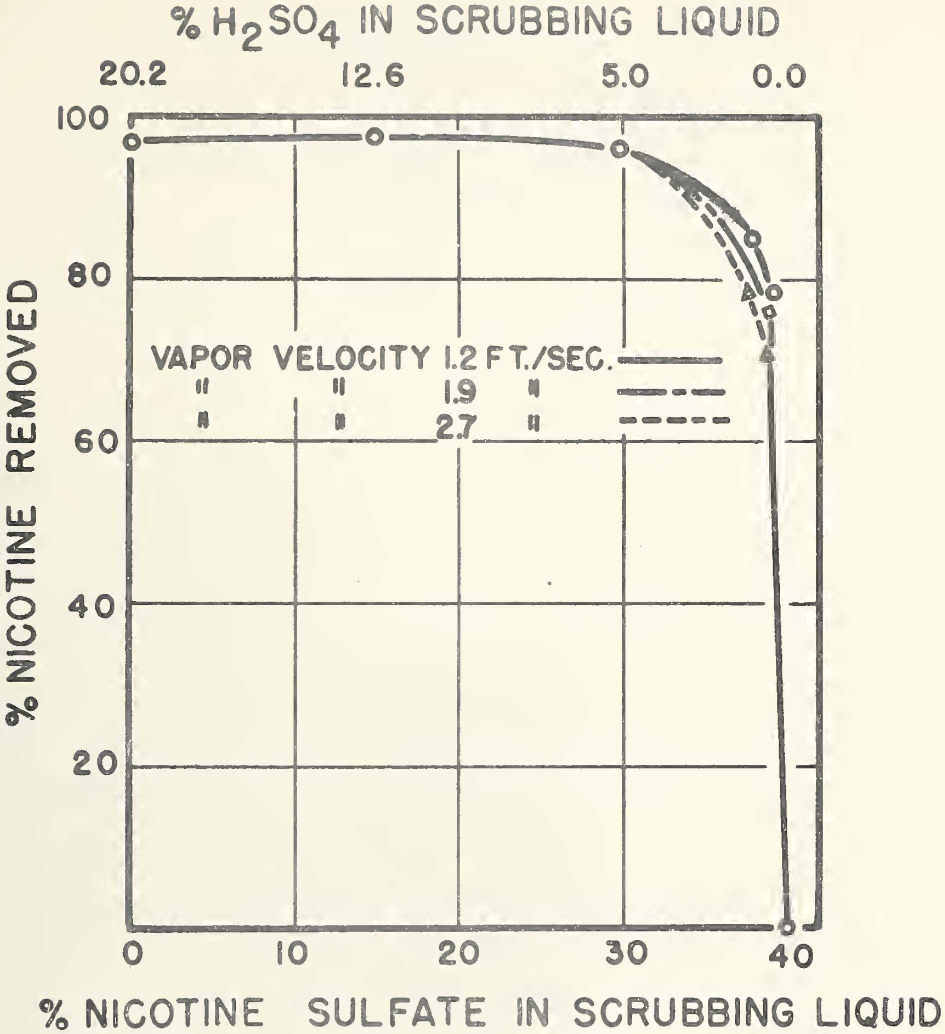

FIG. 4–EFFECT OF CONCENTRATION OF SCRUBBING ACID ON REMOVAL OF NICOTINE (UNPACKED SCRUBBER OF $2\frac{3}{4}$" I.D.)

CONCLUSIONS

Removal of nicotine from steam by scrubbing with sulfuric acid is primarily a chemical reaction, and the need for countercurrent operation is questionable. Therefore, unpacked towers filled with scrubbing liquid can be used instead of a packed tower, which becomes fouled with ammonium sulfate. No circulation of the liquid is required. Since the efficiency of absorption of nicotine falls off rapidly when the sulfuric acid in the scrubbing liquid falls significantly below 5 percent, it is necessary to use two absorption towers in series. When nicotine sulfate reaches a concentration of approximately 40 percent in the first tower, it is drawn off and used as product after the ammonium sulfate crystals are removed by decantation or filtration. The second tower then becomes the first.